# LabNotes Fall 2004

## Lab of Year Award turns 10

By Camille G. Johnson and Rick Mealy

This coming March will close out the 1st decade of the Wisconsin DNR Lab Certification Program's ***Registered Laboratory of the Year Award***. The first year awards were given was 1996 when the Modine Manufacturing Company won the Large Registered Lab Award and


*Also in this Issue:*


- **Exams, Meetings & Training ……**3
- **Program Administration……** 4
  NR149 Revision Update
  NR219 changes approved
  VOC Surrogate Calibration
  Discrete Analyzers
  SDWA: PTs by Method
- **Proficiency Testing……**6
  PT Problem Solving
  PT Deadlines
- **Council Corner……...**7
  G-I-G-O Redux
- **Auditor Notes……**9
  Camille Johnson
  John Condron
- **Drinking Water Focus...**10
  Electronic Reporting Update
- **Wastewater Focus……**10
  e-DMR Becomes Reality
  Reporting Lab IDs
  E. coli Update
  Reporting Solids Data
  New PCB Requirements
- **General Interest……...**14
  ICP: Interference Check-Part II


*Continued on next page*



Contact us at: (608) 267-7633 or LabCert@dnr.state.wi.us
Web Site: www.dnr.state.wi.us/org/es/science/lc

***Labs of the Year,*** *continued.*

the Town of Bloomer Wastewater Treatment Plant won the Small Registered Lab Award.

We initiated this program not only to recognize those laboratories that were going above and beyond the Program requirements, but also to highlight the breadth of demands placed on many of the individuals in these facilities. Some may think, "Aw…they have it easy…those guys only have to test for BOD and TSS", but those that do have no idea of how a small municipality operates. Frequently, the same guy doing the lab work (the BOD and TSS) also has to run the plant, mow the grass throughout the municipality, plow the streets, clean the streets, and perform general maintenance. I've learned of lots of other seemingly unrelated duties that fall to these folks, but perhaps the strangest of them all was an operator who had to cut my audit short because he had to line the baseball fields for a tournament beginning that afternoon.

We checked in with several past winners to get their perspective on how the Awards have changed the Program. The overwhelming response we received is that people appreciate being recognized for their efforts and that the recognition helps to keep you working to improve despite all the demands and a limited amount of time.

We should view the Lab of the Year Awards as a huge success simply because it has helped us to learn as much about registered labs as they have about our requirements. We occasionally hear of friendly competitions within different parts of the state. Once a particular lab wins the award, other, neighboring facilities want that plaque on their walls. Nothing spurs people to go the extra mile like seeing others being rewarded for their efforts.

***… [receiving the award] makes you feel good about what you do, helps with moral and reinforces [the need for] what you do.***

***Albert Kardoskee Jr***
***DePere WWTP (1998)***

Nomination forms for the 2005 Lab of the Year Awards are available from Camille Johnson, WI DNR, 1300 W. Clairemont Ave., Eau Claire, WI 54702. email: camille.johnson@dnr.state.wi.us, **phone**:(715) 831-3272 **FAX**:(715) 839-1605.


**LabNotes**

**Newsletter of the Laboratory Certification Program**

LabNotes is published twice annually by the Wisconsin DNR Laboratory Certification and Registration Program. For information about distribution or to make suggestions for future articles, contact the editor.

John R. Sullivan, Director
Bureau of Integrated Science Services
(608) 267-9753

David Webb, Chief
Environmental Science Services Section
(608) 266-0245

Rick Mealy
LabNotes Editor
(608) 264-6006



This document is available electronically at www.dnr.state.wi.us/org/es/science/lc.

# Exams, Meetings & Training Opportunities

## *Operator Certification Exams*

DNR will hold Wastewater, Drinking Water and Septage Operator Certification exams on May 4, 2005 (postmark deadline April 6, 2005) and November 2, 2005 (postmark deadline October 5, 2005) in DNR Regions around the state. Check the Op Cert. web site for details, as they become available. Application packets will be mailed in February 2005. □

www.dnr.state.wi.us/org/es/science/opcert

## *2005 Conferences & Meetings*

### MWAA Winter EXPO - 40th Anniversary

The Midwest Water Analysts Association has scheduled Winter EXPO 2004 for January 28, 2005 at the Bratstop Banquet Center in Kenosha. Contact Larry Dressel at (630) 369-5586 for info. □

www.midwestwateranalysts.org.

### Government Affairs Seminar

The Government Affairs Seminar (jointly sponsored by Wisconsin DNR, the Wisconsin

Section of the Central States WEA, Wisconsin Wastewater Operators Association, Municipal Environmental Group and Wisconsin League of Municipalities) will be held March 3, 2005 at the Marriott Madison West, in Madison. □

### FET's Environment '05 Conference

The Federation of Environmental Technology's (FET) annual conference will be held March 8, 2005 at the Milwaukee Hilton City Center, in Milwaukee. □

### Spring BioSolids Symposium

The Spring BioSolids Symposium will be held March 15, 2005 at the Holiday Inn, in Stevens Point. □

### Rural Water (WRWA) Annual Conference

The Wisconsin Rural Water Association holds its annual conference March 28 through April 1, 2005 at the Green Bay Regency Suites and KI Convention Center complex. Call (715) 344-7778 or visit their web site for more information. □

www.wrwa.org

### WWA Annual Conference

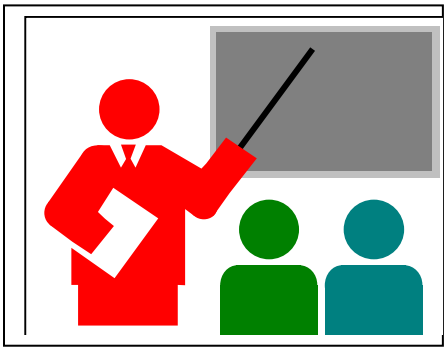
The Wisconsin Water Association (formerly AWWA WS) annual conference is scheduled for September 15 through 17, 2004 in Appleton. Contact Jack Albrechtson at (608) 831-6554 for more information. □

www.wiawwa.org.

### WWOA 39th Annual Conference

The Wisconsin Wastewater Operators Association annual conference is to be held October 4 through 7, 2004 at the Green Bay Regency Suites and KI Convention Center complex. Check the WWOA web site for more details. □

www.wwoa.org



## *Training for Lab Analysts*

| | |
|---|---|
| **Lab Practices/QA-QC Proc.** | April 5, 2005 |
| Tomahawk/WRWA | (715) 344-7778 |
| **Laboratory Analysis 1** | April 5-7, 2005 |
| Chippewa Falls/CTC | (800) 221-6430 |
| **Lab Quality Assurance** | April 27 & 28, 2005 |
| Madison/MATC | |

BTC: Blackhawk Technical College
CVTC: Chippewa Valley Technical College
FVTC: Fox Valley Technical College
NWTC: Northeast Wisconsin Technical College
MPTC: Moraine Park Technichal College
MATC: Madison Area Technical College □

www.dnr.state.wi.us/org/es/science/opcert/training.pdf

# Program Administration

## NR 149 Revision…Where We Are and What's Next

The NR 149 RAC met late summer to evaluate the draft NR 149 that was prepared by the Laboratory Certification Program. The RAC endorsed the product for advancement through DNR's internal processes. The LC&RP met a month later to review and comment on the language that is being proposed. At this time the Group Leaders are merging comments into a single draft, which will receive one final review prior to submittal to the Natural Resources Board.

Please direct all questions and comments to the NR 149 Revision Leaders:

**Diane Drinkman**
(608) 264-8950
Diane.Drinkman@dnr.state.wi.us)
or **Alfredo Sotomayor**
(608) 266-9751
Alfredo.Sotomayor@dnr.state.wi.us). □

## NR 219, Wis. Adm. Code, Update

Chapter NR 219 contains the approved analytical methods for testing wastewater discharges. This code was last updated in 1996. Since then there have been numerous change in the federal rules (40 CFR 136). One of the major changes is the approval of the 20th edition of "*Standard Methods for the Examination of Water and Wastewater*". Other changes include"

- Add test methods for E. coli, enterococci, cryptosporidium, and giardia.
- Update methods from EPA reference SW-846.
- Add test methods for extraction, extract clean up, and quantification of PCBs in sludge.
- Add test methods for pharmaceutical pollutants.
- Add test method for cyanide and absorbable organic halides

The public hearing on the proposed changes was held on May 12, 2004. The Natural Resources Board approved the changes on August 11, 2004. **The effective date for this update is December 1, 2004**. For more information see the Department web site at:
www.dnr.state.wi.us/org/es/science/lc/RULES/NR219.htm

□

## VOC Surrogate calibration

On September 28, 2004, a letter was sent out to all labs currently certified or registered to perform VOC analysis. The purpose of the letter was to inform them of the following:

The Laboratory Certification Program has historically required labs to generate multi-point calibration curves for surrogates in accordance with section 11.4.1.1 of SW-846 method 8000C (7.4.1.1 of method 8000B). This method instructs the user to "… prepare calibration standards at a minimum of five different concentrations…[f]or each analyte and **surrogate** of interest.." The laboratory certification code [NR 149.14(3)(b)] also requires that, "A calibration shall consist of at least 3 standards and a blank except as allowed in approved methods using ion selective electrodes or inductively coupled plasma."

However, recent correspondence with EPA's Method Information Communication Exchange (MICE) service and the Office of Solid Waste (OSW) clarified that the language in method 8000 was not intended to limit calibration options, and upcoming revisions to method 8260 will reflect considerable changes**. In light of advancements in technology and general changes in the science of the analysis, the LabCert program will no longer require multi-point calibrations for VOC surrogates under the following conditions:**

- The allowance is limited to the analysis of VOCs and PVOCs in aqueous (non-drinking water) samples that are not processed through a separate extraction.
- Analysis must be conducted using a sealed vial purge & trap autosampler system (e.g., Archon®, Precept®), and
- The addition of surrogates (and internal standards) must be via auto-injection.

If you have any questions regarding this issue or are interested in further detail regarding the allowance, please contact your laboratory auditor. □

## A Word About Discrete Analyzers

By Rick Mealy

The latest wave in automated chemistry analyzer instrumentation is the "Discrete Analyzer". Discrete Analyzers are currently at the top of the pile that began with the early Technicon auto-analyzer systems. A discrete analyzer is simply an instrument that provides multiple automated chemical analyses to be performed simultaneously on any given sample using micro-volumes of both sample and reagents.

A number of instrument manufacturers have developed their own particular Discrete Analyzer. Some of the more familiar names include Westco's "SmartChem", the KoneLab, the Seal Analytical AQ2, and Lachat Instruments' AP300.

***… instrument vendors must be able to provide you with a letter from the EPA indicating that the chemistries involved are equivalent to those in referenced, promulgated procedures.***

Does Wisconsin Allow Use of Discrete Analyzers?

The Laboratory Certification and Registration Program Code (NR 149) does not provide us with authority to either allow or disallow any analytical instrument. To answer the question, then, we have to re-phrase it in terms of something over which the Program does have authority. The appropriate question to ask is: *"Does the particular Discrete Analyzer use methods approved by the EPA (and the Department)?*"

In most cases, instrument manufacturers have developed micro-chemistry procedures based on promulgated EPA methodologies. It is in their interest however, to request that the EPA review their procedures and issue a letter substantiating that the chemistries are equivalent to those in a promulgated analytical technique.

The bottom line is that instrument vendors must be able to provide you with a letter from the EPA indicating that the chemistries involved are equivalent to those in referenced, promulgated procedures. Auditors will be looking for such a letter, and without one, your lab could be cited for using unapproved methods.

## SDWA Certification Requires PT by Method

Safe drinking water act certified laboratories are required to annually achieve acceptable results on PT samples for each analyte/analyte group and **for each method used to report compliance monitoring results**. Methods used solely for confirmation are excluded. To be certified for an analyte group (e.g., VOCs, haloacetic acids) laboratories must pass 80% of the individual analytes in the PT sample.

The requirement to analyze PT samples by each method used is located in the EPA's "Manual for the Certification of Laboratories Analyzing Drinking Water," 4th ed. March 1997. The Wisconsin Laboratory Certification and Registration Program rule incorporates the EPA Drinking Water Certification Manual by reference (see s. NR 149.21, Wis. Adm. Code). On December 1, 1999, EPA promulgated the requirement for PTs by method in the Federal Register, with an effective date of January 1, 2000. In Wisconsin, implementing the requirement for PTs by method is complicated by the fact that certification is offered by analyte and not by method. However, this does not exempt laboratories from meeting the federally promulgated requirement, since Wisconsin, as a primacy state, holds delegated authority. The Wisconsin Laboratory Certification and Registration Program requires laboratories submitting applications for SDWA analytes to include PTs, MDL studies, and --for organic analytes--IDC studies, for each method listed on the application.

The Laboratory Certification Program will be sending out a status update form to each laboratory currently certified or registered to perform drinking water analyses. Laboratories must report back on these forms the approved methods that they intend to use to analyze drinking water compliance samples. In order to continue to provide compliance data to Wisconsin, laboratories will be required to pass a WS sample from an approved provider for each analyte/analyte group and using each method indicated on the form. Compliance results submitted for any parameter for which a laboratory has not submitted the requisite PT information will not be accepted by the Department.

Please contact Rick Mealy at (608) 264-6006 or richard.mealy@dnr.state.wi.us if you have any further questions this requirement.

# Proficiency Testing

## *Resolving PT Problems*

Rick Mealy

We continue to have troubles with laboratories having to scramble for additional PT samples at the last minute for a number of reasons. Please keep in mind that PT providers are preparing and evaluating samples in accordance with guidance required by NIST. Wisconsin has some differing requirements, however, so it's possible for you to obtain results from a PT provider that indicate all analytes are acceptable, yet the PT is not acceptable (to renew your certification) for Wisconsin. Several of the most typical problems are outlined below:

1. We didn't get your PT results

We all make mistakes. I know I have either misplaced PT results or missed results for one analyte on a page of many. I'm not particularly happy when I discover that I made these mistakes, but I also know I'm not alone. This year, in particular, I recall not receiving a large set of study results (that we should have received) at least once from every major PT provider.

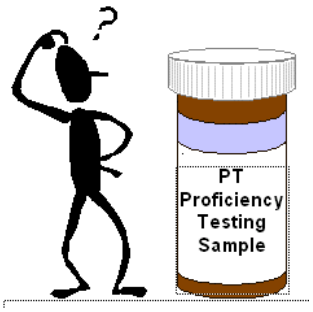
Laboratories should bear in mind that the ultimate responsibility for ensuring that we get PT results on time lies with the laboratory--not the PT provider. PT results are not required to come to us directly from the PT provider, we can accept them from the laboratory…as long as the study has closed.

Mail into the agency sometimes gets mis-routed. To ensure that mail gets directly to one of the LabCert staff, be sure to append the mailcode "**- SS/BW**" after the individual's name. This code tells the mailroom to direct the mail to the satellite office where the LabCert Program resides. Alternatively, have your PT provider e-mail the results directly to us. Finally, all PT results should be sent from the provider to the attention of Rick Mealy. If results are sent to your lab auditor, that individual may assume that I already have a copy and not pass it on.

2. We Grade PT Sample Results Differently

Wisconsin is not a NELAC state and we do have some disagreement over the PT grading protocols outlined in the "National Standards Criteria Document". In fact, under Wisconsin law, we could

***…continued on page 9***




## *Deadlines for Renewal PTs*

Remember that the end of the calendar year signifies the beginning of a new certification year as far as PT samples go. Every PT result with a study closing date of January 1. 2005 or later will apply to certification for the period from 9/1/05 - 6/30/06.

**January 1** PT studies must close after January 1 to be counted for the 2004-2005 certification and registration cycle.

**August 31** Acceptable results must be received by the Department by midnight.

**September 1** Laboratories that did not submit acceptable reference sample results for each test for which they are required prior to September 1 are not renewed for those tests, must cease performing analyses for the analytes, and are required to subcontract the work to a certified laboratory. Reapplication is necessary.

Laboratories must annually achieve acceptable reference sample results for each test for which certification or registration renewal is sought. Reference samples for renewal must be analyzed after January 1 of each calendar year. This office must receive reports from reference sample providers by August 31. For example, if your laboratory wishes to renew its BOD certification for the period beginning September 1, 2005, you would have to analyze and pass a reference sample between January 1and August 31, 2004. Although the current certification period ends August 31, 2005, the program needs sufficient time to generate and distribute certificates to the laboratory community by September 1.

Please direct questions about reference sample requirements to Rick Mealy, Laboratory Certification Chemist at (608) 264-6006, or vie e-mail at richard.mealy@dnr.state.wi.us. □

# Council Corner

*By Paul Junio, Council Chair*

Garbage in, garbage out. I think I first heard this oft-repeated mantra during computer programming classes in the early 80s. It applies to much more than computer programming, and some happenings around the lab have re-enforced this.

Recently, we had a consultant stop by looking for sample containers, some soil jars and a few vials of methanol. Not an unusual occurrence, but when he said he'd be right back in with his samples, the bells started going off. A little reconnaissance found him working in the back of his pick-up truck in the parking lot, presumably transferring soil from something else into the proper containers … while a commercial delivery vehicle was parked in the parking lot with its motor running. When the samples were brought into the lab a short time later, we did all we could do by noting what we saw on the chain (there were more samples than just the 4 containers he had requested, so we couldn't know what samples were transferred).

Another consultant came in with his VOC vials, and they weren't full. He had noticed that the samples were fizzing while he was filling the vials, and he didn't know what else to do.

In both of these instances, the methods of analysis address proper sampling techniques. Unfortunately, I don't think that enough samplers read the methods of analysis, and therefore don't collect samples in the proper manner. Somehow, I imagine that we'll get a phone call based on the first instance, wondering why the trip blank has hits in it (I don't know – a little vehicle exhaust might have something to do with it).

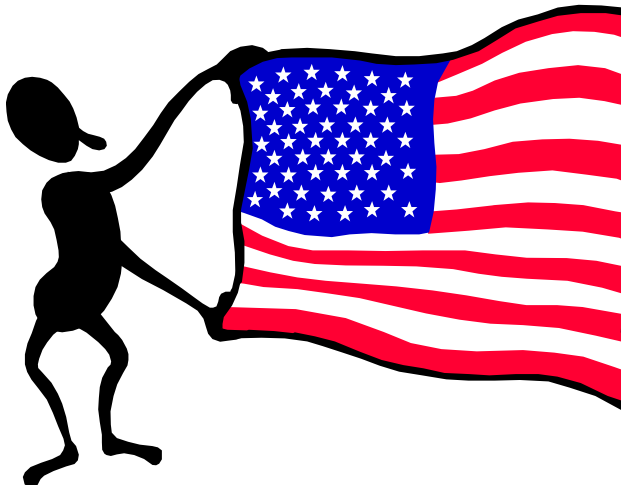
***"Unfortunately, I don't think that enough samplers read the methods of analysis, and therefore don't collect samples in the proper manner."***

Now, I certainly am not advocating that we attempt to certify samplers and/or sampling. There are enough things that look different in the proposed revision to NR149 that I don't think we could get any agreement on how to address sampling. Also, I've seen how the attempts to regulate sampling at a national level have gone (hint – it's not pretty). Part of the problem with attempting to certify sampling is that the appropriate community isn't always represented, nor are they paying attention. That's no fault of theirs – they aren't exactly the target audience of lab certification programs.

Regardless, there are sampling mistakes made. I think they are made more frequently than we realize. Somehow, this needs to be addressed. □

**Current Council Members**

| Representation | Name | Phone # / e-mail |
|---|---|---|
| Commercial Laboratory | Paul Junio ***(Chair)*** | (920) 261-1660 PJunio@testamericainc.com |
| State Laboratory of Hygiene | George Bowman ***(Vice Chair)*** | (608) 224-6279 gtb@mail.slh.wisc.edu |
| Demonstrated Interest in Lab Certification | Marcia A. Kuehl ***(Secretary)*** | (920) 469-9113 makuehl@aol.com |
| Public Water Utility | Katie Edgington | (608) 755-3115 edgingtonk@ci.janesville.wi.us |
| Small Municipal Wastewater Plant | Randy Herwig | (608) 592-3247 rherwig@wppisys.org |
| Industrial Laboratory | Jim Kinscher | (262) 636-1278 j.t.kinscher@na.modine.com |
| Large Municipal Wastewater Plant | Kurt Knuth | (608)222-1201 x293 kurtk@madsewer.org |



# Auditor Notes

## amille Johnson

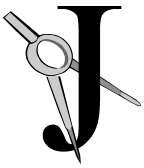
I have been on board with the DNR Lab certification program for four years now. I have seen great progress in the labs I work with, as well as myself. It is a learning process for all of us and one that will never stop due to changing regulations and methods. I hope that more of you are seeing me as a resource now and will continue to contact me with your questions and comments. I truly enjoy travelling around the state and working with all of you. I'd like to touch on a few issues that I have been trying to focus on during my audit visits.

The first topic involves DMR reporting of lab analysis. Many of you send a portion of your samples out to commercial labs for analysis (i.e. metals samples). When you receive the data from those labs and report it to the DNR using your DMR form you want to make sure of two things. First, be sure to enter the correct lab I.D. for each parameter you are reporting. If you did the analysis, it will be your lab ID, if a commercial lab did it then you need to supply that lab's I.D. Next, if the commercial lab has reported any quality control qualifiers (i.e. failed standards, spikes replicates etc.) associated with your data, you are obligated to report those qualifiers on the DMR. It is in your best interest to ensure that these accompany your data so that DNR staff has all the information needed to assess the results.

Another issue involves BOD analysis and pH adjustment. I have encountered some confusion regarding what sample pH requirements are for BOD analysis. According to Standard Methods 20th Edition, 5210 B. 5-Day BOD Test, sample pH has to be within the acceptable range of 6.0 to 8.5. If it does not fall within that range then the sample must be pH-adjusted to fall within a pH range of 6.5 to 7.5. The adjustment is done using minimal amounts of sulfuric acid or sodium hydroxide depending on the adjustment needed (not to exceed a 0.5% dilution of the sample). Any samples that have been pH-adjusted must be seeded. You will then need to run seed controls and adjust the final BOD results using a seed correction factor as you do for GGA samples. Seed is required because you have altered the natural chemistry of the sample. It has been my experience that the majority of routine wastewater samples meet the acceptable range (pH 6.0 to 8.5) and do not need pH-adjustment. Therefore, be sure that any pH adjusting you do is really necessary be sure to seed any sample that has been pH-adjusted.

I hope you all have a great holiday season! Please contact me if you have questions about these reminders or other lab issues.

Email: camille.johnson@dnr.state.wi.us ;
Phone: 715-831-3272 FAX: 715-839-1605 □



## ohn Condron

pH plays a critical role in the analysis of total phosphorus. These next tips apply to manual total phosphorus analysis.

Proper Sample Preservation (all methods)

Unless you plan to analyze for phosphorus immediately (defined by the EPA as within 15 minutes of collection) samples must be preserved at the time of collection by the addition of enough sulfuric acid to drop the sample pH to 2 or below. Preserved samples must be refrigerated at 4°C prior to analysis. *[Note…this preservation requirement applies to ammonia as well]*

pH adjustment prior to digestion

The digestion requires a very acidic solution pH. To ensure that the proper pH is obtained, add 1 drop of phenolphthalein indicator solution to a 50 mL aliquot of sample (*or a volume of sample diluted to 50 mLs with distilled or deionized water*). If the solution color turns pink, add 30% sulfuric acid drop-wise until the solution just clears. This insures that the next acid addition will properly lower the solution pH. Now add 1 mL of 30 % sulfuric acid solution. This is the acid ear-marked for the actual sample digestion.

pH adjustment after digestion

After the sample has cooled following digestion the pH must be in a very specific range for the color development to occur. Dilute whatever sample volume remains after digestion to 30 mL with distilled or deionized water. Then add 1 drop of phenolphthalein indicator to the solution and mix.

…*continued from page 9*

***Auditor Notes…****Continued from page 8*

The solution then must be turned pink by adding 1 N sodium hydroxide (NaOH) and mixed. (This will ensure that in the next step that samples are brought back to being only slightly acidic). Note that the method also instructs the analyst to dilute the digested sample up to a final volume of 100 mLs with deionized or distilled water.

*OK…here comes the tricky part. The next step is part of the analytical method [4500P E](rather than the digestion part, [4500P B.5]) and really assumes that one is simply analyzing ortho-phosphorus directly in a sample without digestion. Also keep in mind that the method assumes that you have diluted the digested sample to 100 mLs and are only using a 50 mL portion for the color development step. It can appear a bit awkward but should make sense if you think it through.*

pH adjustment prior to color development

Pipet 50.0 mL [of the digested] sample into a clean, appropriately sized beaker or flask. Add 1 drop phenolphthalein indicator. If a red or pink color develops add 5N sulfuric acid (H2SO4) solution dropwise to just discharge the color. Finally, add 8.0 mL combined reagent and mix thoroughly.

Food for thought

*One final note about all this. Keep in mind that phenolphthalein only turns pink at a pH of 8.3 or above. Therefore, if you adjust the solution till it turns pink and then add just enough acid to dispel the color, the solution pH is not necessarily acidic!*

Please make sure that you are preserving samples as necessary and neutralizing your samples properly at critical points during the analysis. For questions, please contact your regional certification officer. □


***Resolving PT Problems…****Continued from page 6*

not even refer to this document because it has not been formally published and because any document referenced as a requirement must be subject to public comment.

3. We Can't Accept that PT Sample

Again, a number of labs analyzed samples that could not be used to fulfill certification requirements because of Wisconsin-specific requirements. One of the most common occurrences was failure to analyze a herbicide PT sample that contained enough analytes. Wisconsin requires that Herbicide PT samples contain at least 5 analytes. Several PT providers offer Herbicide samples that do not meet these requirements.

Another recurring problem involves PT samples for GRO and DRO. The Program has developed specific requirements for these samples, and solid matrix PT samples are not allowed for these parameters. Ask your PT provider for the GRO/DRO PT samples that are approved for Wisconsin.

Wisconsin PT Information Sources

Critical PT information can be found on the LabCert website in the following places:

Start by going to the LabCert HomePage…

www.dnr.state.wi.us/org/es/science/lc/…

choose Proficiency Testing (PT) from the left …

www.dnr.state.wi.us/org/es/science/lc/PT/…

From here follow these links:

- …PT Provider Contact Info.pdf
  - for a list of approved PT providers
- …PT Provider Parameter Approvals.pdf
  - for tests they are approved to supply PTs
- …PTGuide.pdf
  - for an overview of PT requirements
- …Index.htm
  - for basic grading and PT requirements
- …PTGradingCriteria.htm
  - for detailed PT grading criteria
- …SpecPTReqs.htm
  - for special PT requirements □

# Drinking Water

## *Electronic Reporting Update*

All SDWA-certified labs will be required to report all public drinking water compliance data to the DNR using an electronic reporting method approved by the Department. Due to a number of circumstances, we won't be able to meet the original goal of having all labs report electronically by January 2005. Several labs have met that goal and are already transmitting electronic data files to the DNR. Others are waiting for the DNR's web-based data entry form, which we expect will become available for use by the end of January. We would encourage all laboratories to contact the DNR to get on the schedule for assistance in coordinating their electronic reporting efforts if they haven't already done so. A letter will be going out to the SDWA certified laboratories with more details in early December. If you have any questions, please contact Gail North at (608) 264-6131 or northg@dnr.state.wi.us.

# Wastewater Forum

## *Electronic DMR Becomes Reality*

The Department of Natural Resources (DNR) recently completed piloting a project to accept electronically submitted long-form Discharge Monitoring Reports (DMR's). Additional types of monitoring forms will be accepted electronically as funding for development becomes available. Many of the 25 facilities who helped pilot the project are currently submitting forms electronically and others are being added as requests come in on first come, first serve basis.

There are two electronic submittal processes to choose from, both of which are performed on a secure web site. The first option allows sample results and comments to be entered on a DMR template that replicates a monthly paper DMR. The second option allows a DMR XML (Extended Mark-up Language) file for a given month to be downloaded, sample data already stored electronically mapped to XML tags in the file, and the file to be uploaded. An advantage of the latter option may be the ability to transmit data reported to permittee by a commercial laboratory without the need to re-key the information.

Once the data is entered using either of the processes, a validation process is run, summary data is calculated, the file is submitted, and a permittee certification statement is created, which is mailed to the DNR. Upon receipt of the certification statement, the original file integrity is verified using security software and the file uploaded to the DNR database.

If you are interested in information regarding this process, Gail Mills can be reached at (608) 266-1387 or gail.mills@dnr.state.wi.us. □

## *Reporting Lab ID Numbers*

The Department of Natural Resources will place more emphasis on recording of the nine-digit number of the laboratory that conducts tests, which are reported on the Discharge Monitoring Reports (DMR's). A similar effort regarding collection of the limits of detection (LOD's) and limits of quantification (LOQ's) was initiated in 2003. The Department will notify permittees which parameters need the certified or registered lab number reported. When the lab number is required and not recorded, compliance staff will follow-up with the facility.

Field tests such as Dissolved Oxygen, pH, and Total Residual Chlorine will not require a laboratory number. Also, laboratories are not currently required to be certified or registered for Fecal Coliform testing, though that may change with proposed revisions to the Lab Certification rules. □

## *Solids Reporting Requirements PCB in Biosolids LOD requirement*

It should be noted that all municipal biosolids, industrial sludge and by-product solids analytical results must be reported on a dry weight basis. Most parameters now include dry weight in their name with the exception of nutrients. Nutrients must also be reported as dry weight values (usually as a percent). However liquid wastewater analytical results to be reported in mg/L are still expected to be as wet weight. As a general rule whenever units specified are ug/kg, mg/kg, or percent, it is expected that results are reported on a dry weight basis. If units specified are mg/L then the report results on a wet weight basis.

++++++++++++++++++++++++++++

There is also a conflict between existing WPDES permits which cite an LOD of 1.0 mg/kg and the new LOD of 0.11 mg/kg specified in Chapter NR 219. However, since the Sampling and Testing Procedures requirements section in permits specifies use of methods specified in Ch. NR 219, those requirements supersede the permit language.

☒ ~~Permit LOD: 1.0 mg/kg~~

☑ **NR 219 LOD: 0.11 mg/kg** □

## *E. coli Update*

By Toni Glymph

In October 2002, Congress passed the Beaches Environmental Assessment & Coastal Health Act (BEACH Act) which mandated all States bordering coastal or Great Lakes waters to adopt *Escherichia coli* (*E. coli*) as the pathogen indicator for water quality standards. It is USEPA's assertion that the detection of E. coli in surface water more accurately indicates the presence of fecal material than fecal coliform. The assumption is that if fecal matter is detected, there is an increased risk of human illness due to the exposure to pathogens responsible for cholera, salmonellosis, shigellosis, gasteroenteritis, infectious hepatitis, dysentery, and many other diseases. Currently, the Department uses fecal coliform as the pathogen indicator to ensure the "Recreational Use" designation is met for surface waters of the state. The primary management tool to achieve this water quality standard is the disinfection policy, which is applied primarily to treatment operations where there is an assumed health risk to humans who may come in contact with the receiving water downstream of a permitted discharge.

Currently, Wisconsin uses a "default" classification whereby all waters of the state are designated as a recreational use water unless otherwise granted a "variance" in NR 104 (Wis. Adm. Code). The Department has not required disinfection from WPDES-permitted discharges to those waters specifically listed as Limited Forage Fish or Limited Aquatic Life. It is assumed that natural low-flow and/or other physical limitations prevent full body immersion and a risk to human and animal health does not exist.

In response to the BEACH Act mandate, the Department convened a Technical Advisory Committee (TAC) in May 2004 to begin the revision of the state water quality standards. The committee has also been tasked with reviewing and revising disinfection policies needed to support the standards. The TAC is evaluating the need to develop more than one recreational use category. This approach would apply the more stringent criteria to recreational areas where full body immersion is likely such as designated beaches. It would also include a "non-recreational" use category for those waters that have been determined through a use attainability analysis, to be unsuitable for recreation.

***What will this mean to WPDES Dischargers?***

Disinfection will be required for discharges to recreational waters and monitoring for E. coli will be required in the permit upon renewal. Disinfection will not be required for non-recreational waters. The TAC is attempting to have a Green sheet package to the Natural Resources Board in January/February 2005. It is our hope to have a new rule in place in time for the 2005 recreational season.

***Plans for the Future***

The BEACH Act also mandated EPA to develop new or revised water quality criteria by 2005. EPA Office of Research and Development is currently conducting epidemiology studies designed to evaluate new rapid indicators of recreational water quality and their relationship to health effects. They are currently evaluating the use of enterococci using the standard method (Method 1600) and *Bacteroides* sp. using novel molecular techniques such as quantitative polymerase chain reaction (QPCR).

The QPCR method is presently being evaluated as a possible alternative to membrane filtration tests. PCR is now a widely used laboratory method for detecting specific DNA (or RNA) sequences that can originate from specific organisms, e.g. fecal indicator bacteria. It does this by making copies of these sequences (amplification) in large enough numbers (e.g. Millions) to allow their detection - usually after the amplification is completed. Quantitative PCR (QPCR) differs from conventional PCR by detecting these copies with a fluorescent probe directly in the instrument as the reaction proceeds. For this reason it is also often called real time PCR. EPA feels that the QPCR method may be useful at this time as an early warning system but confirmation with other methods is still recommended. Results from ongoing epidemiological studies may lead to the development of new criteria for beach closings based on same-day measurements by this method. □

## *New PCB Requirements Effective 12/1/2004*

By Greg Kester

*The following information has been paraphrased from a letter that was sent to all permittees in early December. It highlights new requirements associated with the analysis of PCBs in biosolids (sludge).*

**PCB Analytical methods.**

Either congener-specific analysis or Aroclor analysis shall be used to determine the PCB concentration. The permittee may determine whether Aroclor or congener specific analysis is performed. Analyses shall be performed in accordance with Table EM in s. NR 219.04.

(x) Monitoring and calculating PCB concentrations. The PCB concentration in the sludge shall be determined as follows.

1. Analytical methods. Either congener-specific analysis or Aroclor analysis shall be used to determine the PCB concentration. The permittee may determine whether Aroclor or congener specific analysis is performed. Analyses shall be performed in accordance with the following provisions and Table EM in s. NR 219.04.

a. EPA Method 1668 may be used to test for all PCB congeners. If this method is employed, all PCB congeners shall be delineated. Non-detects shall be treated as zero. The values that are between the limit of detection and the limit of quantitation shall be used when calculating the total value of all congeners. All results shall be added together and the total PCB concentration by dry weight reported.

**Note**: *It is recognized that a number of the congeners will co-elute with others, so there will not be 209 results to sum.*

b. EPA Method 8082A shall be used for PCB-Aroclor analysis and may be used for congener specific analysis as well. If congener specific analysis is performed using Method 8082A, the list of congeners tested shall include at least congener numbers 5, 18, 31, 44, 52, 66, 87, 101, 110, 138, 141, 151, 153, 170, 180, 183, 187, and 206 plus any other additional congeners which might be reasonably expected to occur in the particular sample. For either type of analysis, the sample shall be extracted using the Soxhlet extraction (EPA Method 3540C) (or the Soxhlet Dean-Stark modification) or the pressurized fluid extraction (EPA Method 3545A).

If Aroclor analysis is performed using Method 8082A, clean up steps of the extract shall be performed as necessary to remove interference and to achieve as close to a limit of detection of 0.11 mg/kg as possible. Reporting protocol, consistent with s. NR 106.07(6)(e), should be as follows: If all Aroclors are less than the LOD, then the Total PCB Dry Wt result should be reported as less than the highest LOD. If a single Aroclor is detected then that is what should be reported for the Total PCB result. If multiple Aroclors are detected, they should be summed and reported as Total PCBs. If congener specific analysis is done using Method 8082A, clean up steps of the extract shall be performed as necessary to remove interference and to achieve as close to a limit of detection of 0.003 mg/kg as possible for each congener.

If the aforementioned limits of detection cannot be achieved after using the appropriate clean up techniques, a reporting limit that is achievable for the Aroclors or each congener for the sample shall be determined. This reporting limit shall be reported and qualified indicating the presence of an interference. The lab conducting the analysis shall perform as many of the following methods as necessary to remove interference:

- 3620C - Florisil
- 3640A - Gel Permeation
- 3630C - Silica Gel
- 3611B - Alumina
- 3660B - Sulfur Clean Up (*using copper shot instead of powder*)
- 3665A - Sulfuric Acid Clean Up

□

# General Interest

## *ICP Interference Correction Part 2 - Proper Determination of ICP Interelement Correction (IEC) Factors*

By Rick Mealy

The challenge, in writing this article, is to try to artfully pack a wealth of critical information into 3 or 4 columns of text. In retrospect, that's likely the reason I opted to write about evaluating IECs in the last issue. The evaluation part is really pretty easy…the tough part is in establishing IEC factors in a defensible manner that ensures your evaluation checks will succeed.

Although there's not enough space here to discuss background correction points in detail, we at least have to broach the subject because the data used to generate IECs can also be influenced by selection of inadequate background correction locations. The trick--whenever possible-- is in separating those effects from spectral overlap (which require IEC factors) from problems related to background correction. Simply stated, spectral overlap occurs whenever an emission wavelength of an interfering analyte either directly overlaps that of the target analyte. Alternatively, with significant concentration, if the interferent signal bleeds into the bandwidth associated with the target analyte, spectral overlap occurs.

Figure 1 represents a basic example of concentration-related spectral overlap. As aluminum concentration increases, there is a point at which the aluminum peak "bleeds" into the region where emission measured is associated with beryllium. This leads to an "apparent" beryllium concentration. The closer the emission line of the interferent is to that of the target analyte, the more slope of the plot of interferent concentration versus apparent target analyte concentration approaches one.

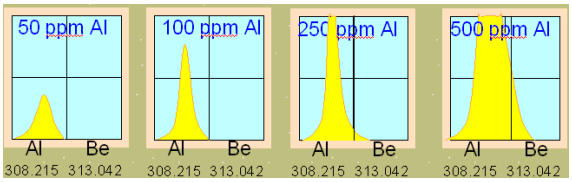



**Figure 1.** Simple illustration of spectral overlap.

Essentially, when a single-element solution of a potential interferent is analyzed, one of three results will be observed for each target analyte: (A) No change in emission counts, (B) a net increase in emission counts, or (C) a net decrease in emission counts. Case (A) is typically--but not always-- representative of an analyte that has no interferent affect upon the target analyte (more on that later). Case (B) is easily seen as a situation involving spectral overlap of some sort, as evidenced by the signal enhancement of the target analyte. Situation (C) is more problematic. Spectral overlap by default means an enhancement of signal attributed to the target analyte (or increase in apparent concentration); therefore an apparent signal suppression cannot be caused by spectral overlap. What we are likely seeing in the affect of aluminum on chromium is an incorrectly positioned background correction point. The other possible explanation is that the determination is being made with existing IEC factors "turned on" and the factors are "over" correcting.

Figure 2 is a set of data demonstrating the apparent enhancement of signal for beryllium with increasing concentrations of aluminum. The parallel bars indicate concentration levels equal to plus (+) and minus (-) the limit of detection (LOD) for beryllium. Note that if the determination were made with only a 50- or 100-ppm aluminum standard, the conclusion might be that this analyte represents situation (A), or no apparent interference effect.

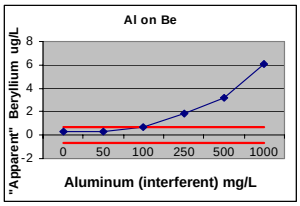



**Figure 2.** *Apparent signal enhancement of beryllium with increasing aluminum.*

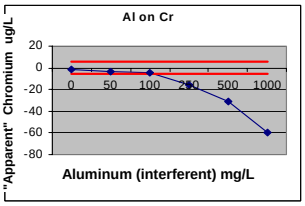



**Figure 3.** *Apparent signal suppression of chromium with increasing aluminum.*

Figure 3 is a set of data demonstrating the apparent suppression of signal for chromium with increasing concentrations of aluminum. The parallel bars indicate concentration levels equal to plus (+) and minus (-) the limit of detection (LOD) for chromium. Again, it is notable that if this determination were made using an aluminum concentration of 100 ppm or below, one might incorrectly conclude that aluminum has no effect on chromium. Since we are measuring emission, and we cannot have negative emission, we can only be seeing the effect of either (1) incorrect IEC factors or (2) an inappropriately positioned background correction point. To properly determine IEC factors, any existing corrections should be "turned off", making (2), background correction, the likely problem.

To further illustrate the importance of background

*Continued on next page.*

correction point selection, two different scenarios must be considered. The first (Figure 4) is the case in which the background correction point chosen perfectly coincides with an emission line associated with a relatively uncommon element. In Figure 4, we see that the background correction point is acceptable as long as the unsuspected interfering element is not present in a sample (Fig. 4a). Because the unsuspected element has an emission line so close to that of the correction point, any emission measured at this location (Fig. 4b,c) is subtracted from the actual target analyte emission counts. Particularly if the target analyte is not present, this can lead to negative concentrations. The extent to which negative apparent concentration is recorded varies proportionally with an increase in concentration of the unsuspected interferent.

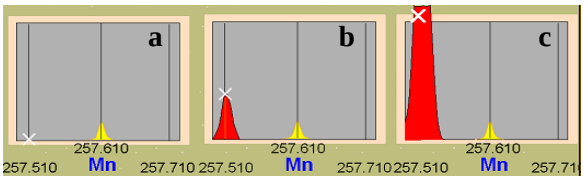



**Figure 4.** *Background correction point set on an emission line of a relatively uncommon element.*

Even if the background correction point for any particular element is not adjacent to any emission lines associated with other elements, similar problems can arise (Figure 5). In Figure 5a, we see that a small amount of an analyte close to the background correction point (x) does not affect correction. With increasing concentration (Figs. 5b,c), however, emission from an analyte with a line close to that of the background correction point (x) can "bleed" into that region causing an elevation in background emission subtracted from the target analyte.

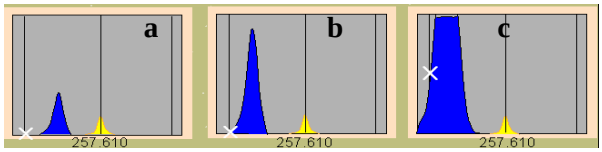



**Figure 5.** *Background correction point set adjacent to an emission line of a relatively common element.*

In all cases, it is important to remember that all analytes respond with differing emission intensities per unit concentration. For one interferent, even the smallest concentration may affect the response of a specific target analyte, while another may need to be present at extremely high levels before any significant impact is observed. Only an adequate interference identification program will provide the answers.

So…what constitutes an "adequate interference identification program"? There are three key parts:

- Identifying “interferents” to be tested
- Determining interferent concentration(s) to test
- Calculating IEC factors

**What “interferents” need to be tested?**

Both methods 200.7 (4.1.4) and 6010 (4.1.2) direct the user to "Table 2", which translates to 17 elements for method 200.7 and 10 for 6010. Elements shared by both methods are: Al, Fe, Cr, Cu, Mn, Ni, Ti, and V. Aluminum and iron are important as two of the four major cations. Although 6010 drops calcium and magnesium (because little or no interferences have been reported for most common analytes using published emission lines), it may be beneficial to include them due to their predominance in most environmental samples.

Initially a lab should have data to demonstrate that interferences from every analyte routinely encountered in samples analyzed have been evaluated for potential effects upon each target analyte the lab reports.

**What concentration of interferent should be tested?**

Both 200.7 and 6010 suggest 100 ppm for non-routine analytes, but studies have been shown that better information is obtained from analyzing each interferent at several concentration levels over a specific range. While this approach certainly means more effort, it also provides the best information. For the four major cations (Al, Fe, Ca, Mg) concentrations as high as 1000 ppm may need to be tested. For less common analytes, much lower concentrations 10 to 100 ppm are likely appropriate. The most important thing to remember is that your IECs are only valid up to the concentrations that have been tested. It's also important that the interferent concentration tested be high enough to generate an "apparent" target analyte concentration above the analyte's limit of quantitation to be certain that the correction factor is appropriate.

**Calculating inter-element correction (IEC) factors**

IEC factors are, quite simply, the amount of "apparent" target analyte concentration per unit concentration of interfering analyte. If a 500 ppm aluminum (Al) standard yields a 50 ppb "apparent" arsenic (As) concentration, then a correction factor (IEC) of -0.1 ug/L must be applied for every ppm Al quantitated in actual environmental samples. Thus if a sample is found to have 100 ppm of Aluminum in it and 11 ppb of arsenic, the arsenic result must be corrected for aluminum interference by 11 - (100 x 0.1) for a corrected arsenic concentration of 1 ppb. □

# 2005 Wisconsin DNR Registered Lab of the Year Nomination Form

The Wisconsin Department of Natural Resources Registered Lab of the Year Awards annually recognize registered laboratories for their outstanding commitment to producing high quality data. One award is presented in each of two categories: Small Facility and Large Facility. Small facilities include municipal wastewater treatment laboratories with a flow of less than 1 mgd, or labs that perform limited types of testing (e.g., BOD, nitrogen, phosphorus, and solids). Large facilities may include major municipal wastewater treatment laboratories with flows greater than 1 mgd, labs that perform tests of greater complexity (e.g., metals, PCBs, VOCs) or labs that process a large volume of samples annually.

Nominees for the award must be *registered* facilities located in the State of Wisconsin. Certified laboratories will not be considered. Anyone, including DNR staff, can nominate a laboratory for one of the awards, but laboratories may not nominate themselves. There is no limit on the number of times that a laboratory may be nominated, and a laboratory may be nominated for (or receive) an award in consecutive years. In the event that insufficient nominations are received for either category, the Department reserves the right to not issue either award.

To nominate a registered laboratory for the 2005 Lab of the Year Award, complete the following form and include a summary of no more than three pages describing the reasons why you are nominating the laboratory for the award. Be sure to address the following considerations in your summary (please note - all considerations do not necessarily have to be addressed for a laboratory to be chosen to receive the award):

**Nomination Considerations:**

- Does the laboratory demonstrate a commitment to exceeding the minimum requirements for compliance with Department rules and guidance?
- Has the laboratory demonstrated a high level of commitment to correcting instances of non-compliance?
- What measures does the laboratory take to ensure the production of high-quality data?
- Does the laboratory's quality assurance program ensure that quality control data is used to evaluate and improve laboratory procedures?
- For which other practices or achievements should the laboratory recognized?

Completed nomination forms must be received by December 31, 2004 in order for the candidate to be considered. A nomination committee will decide the Award winners. Please send the completed nomination form to: Lab of the Year Award, c/o Camille Johnson, WI DNR, 1300 W. Clairemont Ave., Eau Claire, WI 54702 or by FAX at (715) 839-1605.

**Category:** ☐ **Small Registered** ☐ **Large Registered**

**Name of Laboratory Nominated:** _____

**Laboratory Director:** _____

**Laboratory Address:** _____

**Laboratory Phone #:** _____

**Nominator (your name):** _____

**Your Affiliation with Nominee:** _____

**Your Address:** _____

**Your Phone #:** _____

**LabNotes – Fall 2004, Volume 19, Issue 2**

Wisconsin Department of Natural Resources
101 South Webster Street
P.O. Box 7921
Madison, WI 53707-7921

Presorted Standard
U.S. Postage
Paid
Madison, WI
Permit 906